

**DEVELOPMENT OF N-TYPE SPIN-ON DOPANT FOR SILICON
DEVICES**

by

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**Thesis submitted in fulfilment of the requirements
for the degree of
Master of Science**

May 2009

ACKNOWLEDGEMENTS

First and foremost, I would like to express my gratitude to Allah S.W.T, since with his blessing; I had been able to finish my thesis successfully. It is my pleasure to express sincere thanks to my main supervisor, Prof. Kamarulazizi Ibrahim for all his guidance and supervision throughout the course of my research. I would also like to thank my co-supervisor, Assoc. Prof. Azlan Abdul Aziz for his support and willingness in helping me to expand my knowledge in this field of research. Not to be forgotten to Dr. Magdy H.Mourad for his additional advice and help.

Furthermore, I would like to take this opportunity to express my thanks to the technical staff from NanoOptoelectronic Research and Technology Laboratory (N.O.R) for their kindness and technical support. Apart from them, I would also like acknowledge my research colleagues especially Y.K.Sin, P.K. Ooi, C.W. Chin and Osama for their assistance in research and ingenious ideas during discussion also provide valuable support.

I also wish to express my utmost gratitude to UiTM for allowing me the chance to be doing what I feel is a massive challenge but ultimately fruitful endeavor in completing this research and subsequently my future lecturing undertaking.

Last but most importantly, I wish to acknowledge the care and encouragement given by my loving husband, my parents and all family members. Thank you very much for supporting me in so many ways from the beginning to the end.

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LIST OF MAJOR ABBREVIATIONS

Al	Aluminium
DI	Deionized
FTIR	Fourier Transform Infrared
H ₃ PO ₄	Phosphoric acid
HF	Hydrofluoric acid
HMDS	Hexamethyldisilazane
In	Indium
IPA	Isopropanol
IR	Infra red
I-V	Current-Voltage
N ₂	Nitrogen
O ₂	Oxygen
PR	Photoresist
RCA	Radio Corporation of America
RH	Relative humidity
Si	Silicon
SOD	Spin-on dopant
SOG	Spin-on glass
TEOS	Tetraethylorthosilicate
TMOS	Tetramethoxysilane
UV	Ultra Violet

LIST OF SYMBOLS

B	Magnetic field
$C.F$	Correction factor
D	Diffusion coefficient
E	Electric field
E_c	Conduction band edge
E_F	Fermi level
E_{Fm}	Fermi level of metal
E_{FS}	Fermi level of semiconductor
E_g	Band gap
E_m	Maximum value of electric field
E_v	Valence band edge
F	Force
I	Current
I_0	Saturation current
J	Diffusion rate
k	Boltzmann's constant
k_s	Dielectric constant of silicon
M	Molarity
m^*	Effective mass
N	Carrier concentration
n	Ideality factor
n	Electron
N_0	Surface concentration
N_a	Acceptor carrier concentration
N_B	Background carrier concentration
N_d	Donor carrier concentration
n_i	Intrinsic concentration of electron
n_n	Electron on the n-material
p_p	Holes on the p-material
p	Hole
q	Electron charge
Q	Symmetry factor
Q	Dose
r	Ratio
R^*	Band area ratio
R_S	Sheet resistance
R_H	Hall coefficient
s	Probe spacing (cm)
t	Time
T	Temperature
v	Velocity
V	Voltage
V_{bi}	Built-in voltage
V_H	Hall voltage
w	Width

W	Total width of the depletion region
x	Junction depth
x_n	Depletion width of n-side
x_p	Depletion width of p-side
μ	Mobility
τ	Time between scattering event
μ_H	Hall mobility
χ	Electron affinity
ϵ_0	Permittivity of vacuum
ϵ_s	Permittivity of a semiconductor
ϕ_b	Barrier height
ϕ_m	Metal work function
ϕ_s	Semiconductor work function
ρ	Resistivity

PEMBANGUNAN PENDOP PUTARAN ATAS JENIS-N UNTUK PERANTI SILIKON

ABSTRAK

Di dalam penyelidikan ini, kerja-kerja lebih difokuskan kepada penyediaan pendopan putaran jenis n (*SOD*) menggunakan teknologi *sol-gel*. Tujuan utama penyelidikan ini adalah untuk menyediakan SOD dengan kepekatan pendopan di antara 10^{16} kepada 10^{20} sm^{-3} . Kepelbagaian kepekatan ini adalah amat penting memandangkan peranti yang berbeza memerlukan kepekatan pendop yang berbeza. Fokus dan cabaran utama di dalam penyelidikan ini ialah untuk menentukan komposisi bahan kimia dan keadaan yang jitu dimana dapat memenuhi kriteria penyediaan pendopan putaran jenis n (*SOD*) yang mempunyai ciri-ciri yang hampir sama ataupun lebih baik daripada yang berada di pasaran.

Pelbagai alatan pencirian telah digunakan untuk mengkaji ciri-ciri SOD. Pengukuran Kesan Hall telah dilakukan untuk mendapatkan rintangan keping, kerintangan, kelincahan, kepekatan kepingan dan kepekatan pembawa. SOD dengan kepekatan fosforus yang berlainan berjaya diperolehi dengan menggunakan teknologi *sol-gel* dengan kepekatan pendopan di antara 10^{16} kepada 10^{20} sm^{-3} . Setiap SOD mempunyai resepi tersendiri bergantung kepada kepekatan fosforus.

Penduga-empat titik kemudiannya digunakan mengesahkan rintangan keping dan kerintangan yang telah diukur oleh Kesan Hall. Perbezaan antara rintangan keping dan kerintangan yang diukur oleh Kesan Hall dan penduga empat titik adalah sangat kecil. Selain daripada alatan di atas, spektrometer Fourier transformasi inframerah juga digunakan untuk mengkaji ikatan dan komposisi SOD. Komposisi dan ikatan dalam SOD boleh diperolehi daripada penyerapan spektra inframerah.

Untuk membuktikan keberkesanan SOD yang telah disediakan di dalam makmal, larutan itu digunakan dalam fabrikasi peranti iaitu simpang p-n (diod). Sistem arus-voltan (I-V) menunjukkan diod yang terhasil menggunakan SOD yang telah disediakan di dalam makmal dan SOD yang berada di pasaran mempunyai lengkung yang hampir sama.

Kajian ini menunjukkan yang SOD yang telah didop dengan kepekatan fosforus yang berbeza telah berjaya dihasilkan menggunakan teknologi sol-gel. SOD boleh disediakan di dalam makmal tanpa perlu untuk membeli SOD di pasaran. Namun, kajian perlu diteruskan untuk pendop putaran jenis-p.

DEVELOPMENT OF N-TYPE SPIN-ON DOPANT FOR SILICON DEVICES

ABSTRACT

In this research, works are focused on the preparation of n-type spin-on dopant (SOD) using sol-gel technology. The main aim of this research is to prepare n-type SOD with doping concentration in the range of 10^{16} to 10^{20} cm^{-3} . This various doping concentration is very important as different type of device need different dopant concentration. The major focus and challenge of the research is in finding the exact ratio of chemical and conditions that would satisfy the preparation criterion of n-type SOD that is on par or perhaps even better than those available commercially.

Various characterization instruments were used to investigate the properties of SOD. Hall Effect measurement was done to obtain the sheet resistance, resistivity, mobility and sheet and bulk concentration of prepared SOD. SOD with different phosphorus concentration have been successfully attainable using sol-gel technology with doping concentration of 10^{16} to 10^{20} cm^{-3} . Each SOD has its own recipe accordance to the phosphorus concentration.

Four-point probe was then used to verify the sheet resistance and resistivity measured from Hall Effect. The difference between sheet resistance and resistivity measured by Hall Effect and four-point probe is insignificant. Apart from the above mentioned instruments, Fourier transform infrared (FTIR) spectrometer has also been used to study the bond and composition of SOD. Composition and bond in SOD can be determined from absorbance IR spectra.

To prove the effectiveness of SOD prepared in the laboratory, that solution was used in device fabrication which is p-n junction (diode). Current-voltage (I-V)

characteristic system showed that the diode which uses prepared SOD in the lab and commercial SOD have almost similar behavior.

This research shows that SOD doped using different phosphorus concentrations have been successfully prepared using sol-gel technology. SOD can be prepared in the laboratory thus eliminating the need to buy commercial SOD anymore. However, further research need to be done for p-type SOD.

CHAPTER 1

INTRODUCTION

1.1 Research motivation

SOD, although widely available in the market, has always been a cost-sensitive material to the semiconductor industry. Usage of SOD in laboratory and for academic purposes has seen the material to be highly regarded and pivotal in attaining the desired output and results especially in the doping process. Nevertheless, the importance of SOD has seen the price of the material to escalate. In addition to that, several other factors contributes to the unattractiveness of market supplied SOD. For example, SOD supply has always been unavailable in small quantities that usually suit the usage and application in academic laboratories. Market supplied SOD has also been scarce in various level of concentration, which usually are the requirement for experimentation usage in classrooms in Universities around the world, especially in Malaysia, where the semiconductor supply chain is heavily dependent on the demand by the industry.

SOD is also notorious for its short shelf life. Coupled with its supply that is quite often in bulk and also its sporadic usage in laboratory, more often than not the material ended up discarded and wasted.

These issues may seem trivial yet it has dogged the academic world for ages and has been a constant contributor to the increasing cumulative costing in maintaining a science laboratory in educational institutions.

With this research experience, the researcher hope to be able to look at other hindrances and challenges in the researcher's future undertaking and later contribute to

the solution finding exercise on other aspects of the running of a science faculty in a university.

1.2 Research objectives

The first goal of this research is to prepare n-type SOD with a various dopant concentration in the range of 10^{16} to 10^{20} cm^{-3} for silicon devices. This various concentration is very important as different type of device need different dopant concentration. The major focus and challenge of the project is in finding the exact ratio of chemical and conditions that would satisfy the preparation criterion of n-type SOD that is on par or perhaps even better than those available commercially.

Another objective of this research is to reproduce SOD in a classroom using the sol-gel technology to cater to the need of students and researchers doing experiments about the doping process. It is hoped that this research will lead to the possibility of preparing the vital material in a most cost effective manner and optimizing the produced quantity specifically for the needed requirement for study thus eliminating wastages and over procurement of the said material.

Following the intensive investigations about SOD, various instruments were used to characterize prepared and commercial SOD. Each instrument was used to compare quality and properties between prepared and commercial SOD.

Finally, to prove the effectiveness and its performance, the prepared SOD needs to be tested in device fabrication. P-n junction (diode) was chosen to test prepared and commercial SOD. The ease of fabrication, simple experimental setup and the availability of characterization tools for measuring the performance of the diode are the main reasons for choosing diode as a device to test the prepared and commercial SOD.

1.3 Outline of the Thesis

The content of this thesis is organized as follows:-

Chapter two encompasses types of dopant, phosphorus dopant and method of doping, application of phosphosilicate, as well as selection method and recipe for the research. Chapter three will cover SOD related matters and theory that are relevant to the work in this research. Chapter four is devoted to the instrumentation employed in this work. Some principles and theories underlying the operation of the instruments are covered in this chapter. Chapter five will consists all process and methodology used in this work which includes sample preparation and characterization. Furthermore, this chapter includes samples usage in this research. This chapter also presents step by step procedure for all work in this research. Continuation from chapter five, chapter six will interpret the characterized data from some interesting point of views. Analysis and comments on the results were also given in this chapter. Last but not least, the summary for the entire work will be expressed in chapter seven. Closing remarks and some suggestions for continuation work is also included.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this chapter, an overview of types of dopant is presented. The review mainly focuses on the phosphorus dopant and method of doping. An application of phosphosilicate is also include in this chapter. Furthermore, this chapter also consist selection of method and recipe for this research.

2.2 Types of dopant

Boron, arsenic, phosphorus and antimony, among other substances, are commonly used dopants in the semiconductor industry. There are two types of dopants which act as a donor and acceptor (Singh, 2001).

Dopants for silicon and germanium, group IV semiconductors:

Donors: group V atoms: antimony, phosphorus, arsenic

Acceptors: group III atoms: boron, aluminium, gallium

Dopants for gallium arsenide, a group III-V semiconductor:

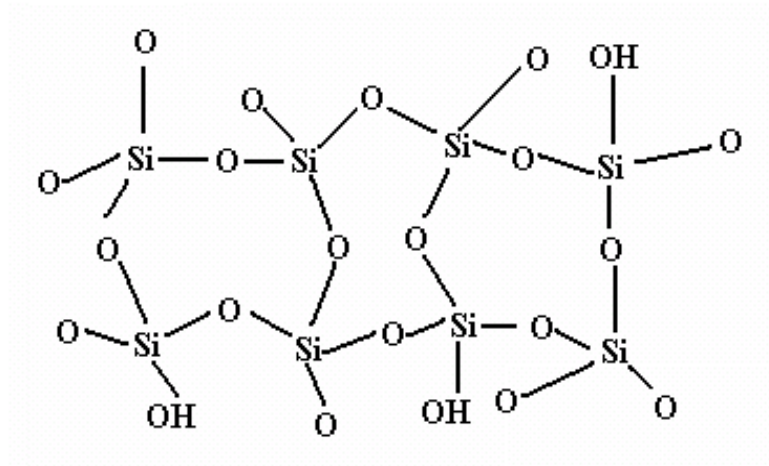
Donors: group VI and group IV atoms: sulfur, selenium, tellurium, silicon

Acceptors: group II and group IV atoms: magnesium, zinc, cadmium, silicon

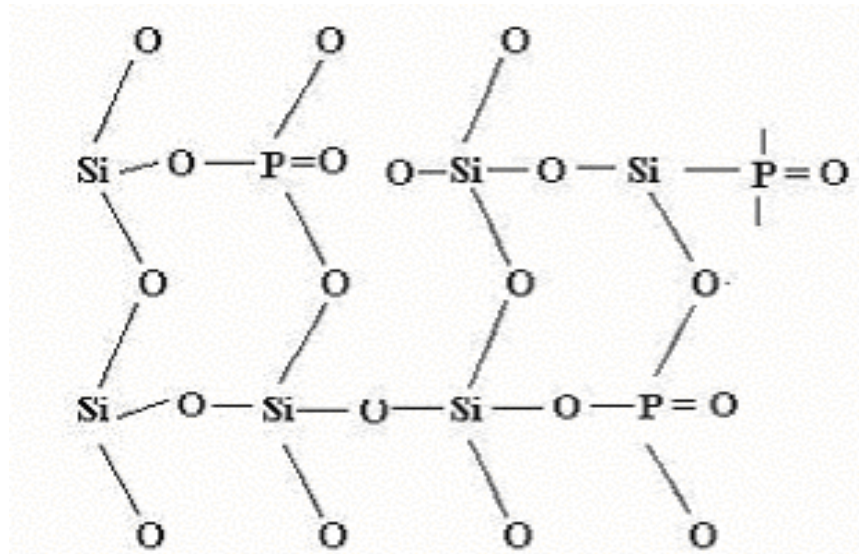
2.3 Phosphorus dopant and method of doping

Many research have been done on phosphorus dopant. Normally, phosphorus dopant material used to dope into silicon is silicate based compound and usually called

phosphosilicate. Phosphosilicate fabrications start with fabrication of spin-on glass (SOG) and then modified by adding phosphorus inside SOG (Chul & Seong, 1994). A rough description of the SOG and phosphosilicate molecular structure is presented in figure 2.1 (a) and (b) respectively. The dopant source can be in solid, liquid or gas.



(a)



(b)

Figure 2.1: Molecular structure of (a) spin-on glass (b) phosphosilicate (Ergul, 2005)

The doping process can be carried out using a number of methods of which the most commonly employed are chemical vapour deposition (CVD) method, ion implantation method and spin-on dopants (SOD) method.

There are two steps involved in CVD method which are pre-deposition and drive-in steps. During pre-deposition, the diffusant source is transported to the substrate using a carrier gas, resulting in the formation of a dopant-containing film on the silicon surface (Teh, 1988). In the subsequent drive-in step, the predeposited substrate is introduced into diffusion furnace at elevated temperature for a period of a few minutes to several hours.

Tenney and Ghezze (1973) studied about phosphorus doping using CVD method. Phosphosilicate was deposited by passing argon (Ar) diluted mixtures of silane (SiH_4), phosphine (PH_3) and oxygen (O_2) over silicon wafers heated to 300-700°C. For instance, with flow rates of 3800 $\text{cm}^3 \text{ min}^{-1}$ Ar, 40 $\text{cm}^3 \text{ min}^{-1}$ O_2 , 150 $\text{cm}^3 \text{ min}^{-1}$ SiH_4 (1% in Ar), and 13 $\text{cm}^3 \text{ min}^{-1}$ PH_3 (1% in Ar), a 1.0 μm thick film of phosphosilicate was deposited in 35 minutes at 400°C. Alexieva, et al. (1986) deposited phosphosilicate using plasma enhanced chemical vapour deposition (PECVD). Phosphosilicate were deposited onto a silicon wafer in a plasma reactor from the reaction of SiH_4 , N_2O , PH_3 and O_2 . The temperature was 380°C, the specific pressure was 0.86 Torr and the power density was $6 \times 10^{-3} \text{ Wcm}^{-2}$.

Besides that, research was done by Bantoiu and Pavalescu (1990). Films of phosphosilicate (0.2 μm thickness) were deposited on silicon substrate in a rotary reactor at atmospheric pressure and temperature of 400°C in SiH_4 - PH_3 - O_2 - N_2 system. Furthermore, phosphosilicate has also been deposited by Poenar, et al. (1996). Phosphosilicate layer were deposited on silicon wafers in a three-zone hot-wall resistor-

heated low pressure chemical vapour deposition (LPCVD) reactor. The deposition temperature, the pressure and the oxygen flow had values of 425°C, 200 mTorr and 200 sccm respectively. Doping was supplied using PH₃ diluted with SiH₄. Kim, et al. (2001) used an almost similar source with Poenar, et al. (1996) but they used atmospheric pressure chemical vapour deposition (AP-CVD) instead of LPCVD. Hsiao, et al. (2005) then deposited phosphosilicate layer with gas sources of SiH₄, PH₃, O₂ and Ar at the flow rates of 60,50,170 and 70 sccm, respectively, at about 400°C in high-density plasma chemical vapour deposition (HDP-CVD).

On the other hand, ion implantation affords an alternative means of introducing dopants and other atoms into the near-surface region of a semiconductor. In ion implantation, an impurity is introduced into the semiconductor by creating ions of the impurity, accelerating the ions to high energies and then literally shooting the ions into the semiconductor (Pierret, 1996).

There are many researchers who studied about doping phosphorus using ion implantation method at different energy and conditions. One of the research reported that phosphorus were implanted at energy of 100 keV. The dose was varied from 10¹³ to 10¹⁶ cm⁻² (Hwang, et al., 1996). Another research related to this topic was done by Capano, et al. (2000). The energy/dose conditions for the phosphorus implants were 360 keV / 1.5 X 10¹⁵ cm⁻², 220 keV/1.1 X 10¹⁵ cm⁻², 100 keV/8.0 X 10¹⁴ cm⁻², and 30 keV/ 6.0 X 10¹⁴ cm⁻². Tetelbaum, et al. (2003) doped P ion at energy of 150 keV with condition of (0.1-300) X 10¹⁴ cm⁻². Ion implantation of ³¹P⁺ ion beam was also performed by Yamamoto and Itoh (2006). Trimethylphosphine (TMP) was used as the source gas for the phosphorus ions. The energy of the phosphorus ions was 30 eV, which

is the displacement energy of atoms out of their lattice site in silicon at room temperature.

Moreover, spin-on dopants refers to solution of dopants containing silicate in alcohol which is also been called phosphosilicate. It can be applied by spinning, spraying or dip-coating methods. Application of spinning using photoresist spinner is a preferred method because the thickness of the coating can be controlled by varying the spin speed (Teh, 1988). Normally, for spin-on dopant, phosphosilicate is prepared using sol-gel technology.

Sol gel processing is a chemical synthesis of oxide involving hydrolizable alkoxides that undergo a sol-gel transition. Generally it refers to a low-temperature method using chemical precursors that can produce ceramics and glasses. In most of the sol- gel processes for preparing microporous membranes, a stable sol is first prepared as an organometallic oxide precursor, followed by the addition of acid for peptization (Hsieh, 1996). In sol-gel process, a minimum critical amount of certain acid is needed to peptize the hydroxide to a clear sol and in order to form a stable dispersion of particles in the sol (Lee & Pope, 1994).

Organic solvents such as ethanol, methanol, isopropanol, etc are also added in sol gel processing as they are allowed to control the reaction of alkoxide precursors with water, and hence to direct with more flexibility the structure of sol gel products (Mulder, 1996). It is also added to enhance the adhesion of coating to the support and is used to slow the hydrolysis rate and thus stabilize the alkoxides to the formation of well-dispersed particles in sol to the formation of clear gel. If the hydrolysis rate is faster, it will lead to the precipitation of the sol (Lee & Pope, 1994). A sol is a colloidal suspension of solid particles in a liquid while gel is a porous 3-dimensionally

interconnected solid network that expands in a stable fashion throughout a liquid medium (Brinker & Scherer, 1990).

For spin-on dopant, phosphosilicate should remain only on sol phase before it is applied to the wafer. However, the SOD/phosphosilicate goes through a sol-gel transition upon coating on the substrate. It is observed that the solution film undergoes a sharp increase in viscosity. If the substrate has been handled properly, it is now covered uniformly by a tacky gel. In the systems described above, the sol-gel transition is reached when one-phase liquid becomes a two-phase alcogel, solid plus liquid. The alcogel is an oxide polymer that condenses in the presence of solvent. The transition in alcogels is irreversible and occurs with no change in volume. The time of the transition depends on the chemistry of the solution. That tacky gel will be dried gel after baking process (Nguyen, 1999).

Many research had been done in relation to the preparation of phosphosilicate using sol-gel technique with different conditions, methods and recipes. One of the research done was by Szu, et al. (1992). Three series of phosphosilicate were prepared using phosphoric acid (H_3PO_4), triethylphosphate ($\text{PO}(\text{C}_2\text{H}_5)_3$) and trimethylphosphite ($\text{P}(\text{OCH}_3)_3$) respectively as precursors of phosphorus. In all cases, tetraethoxysilane (TEOS) was the source for silica. Phosphosilicate were prepared by mixing two solutions which is solution A and B. Solution A is a mixture of TEOS and methanol and solution B contain water and appropriate amounts of the phosphorus precursors. Solution A and B were subsequently mixed together. Nitric acid (HNO_3) was added to the mixed solutions.

Another research done was by Kim and Tressler (1994). In their work, the TEOS and H_3PO_4 were used as raw materials. Because the number of hydroxyl groups in

phosphoric acid is sufficient to completely hydrolyse TEOS, no water was added in the sol-gel process. To slow down the gelation process, TEOS and H_3PO_4 were diluted with ethanol before they were mixed. Besides that, Chul and Seong (1994) also had prepared phosphosilicate. The starting material was TEOS dissolved in an organic solvent which contains isopropanol, acetone and ethyl alcohol. TEOS is hydrolyzed by water under a catalytic reaction. An organic acid was used as a catalyst. Then, the solution was added with phosphorus pentoxide dissolved in isopropanol.

Moreover, the research was also done by Fernandez-Lorenzo, et al. (1994). Equal volume of TEOS and ethanol containing the phosphate precursor were mixed. Hydrolysis and condensation were performed by the addition of the appropriate amount of water. Two different phosphate precursors were used, $\text{PO}(\text{C}_2\text{H}_5)_3$ and H_3PO_4 . Solid anhydrous H_3PO_4 (Fluka) was used in order to study the role played by the phosphate with TEOS before hydrolysis was carried out. Nguyen (1999) had fabricated phosphosilicate by adding TEOS, water, phosphoric acid, IPA and acetone.

The research related to the fabrication of phosphosilicate continued to be done by D'Apuzzo, et al. (2000). Phosphoryl chloride (POCl_3) and TEOS were used as starting materials in the sol-gel preparation. A solution of TEOS in anhydrous ethanol (EtOH) was prepared and hydrolyzed at room temperature using water and concentrated hydrochloric acid (HCl). This solution was then mixed with a solution of POCl_3 in an anhydrous ethanol. The final solution was then diluted with EtOH .

Matsuda, et al. (2001) synthesized phosphosilicate from TEOS and various kinds of phosphorus-containing compounds such as H_3PO_4 , triethylphosphate ($\text{PO}(\text{C}_2\text{H}_5)_3$) and 2-(diethoxyphosphoryl)ethyltriethoxysilane (DPTS) by the sol-gel method. TEOS was diluted with EtOH and hydrolyzed with water containing HCl while

left stirring at room temperature. An appropriate amount of H_3PO_4 , $\text{PO}(\text{C}_2\text{H}_5)_3$ or DPTS was added to the hydrolyzed solution and stirred at room temperature.

Massiot, et al (2001) then prepared phosphosilicate by a sol-gel process, using TEOS and H_3PO_4 as precursors. TEOS was dissolved in EtOH with TEOS: EtOH ratio of 1:4. Distilled water was then added and the solution was stirred at room temperature. After that, the appropriate amount of H_3PO_4 and water were added. Clayden, et al. (2005) and Aronne, et al. (2005) used similar material and techniques to prepare phosphosilicate. They mixed TEOS, water, HCl, EtOH and POCl_3 . TEOS was hydrolyzed at 50°C without any alcoholic solvent using HCl as catalyst. This solution was left to cool to room temperature and then was mixed with a solution of POCl_3 in anhydrous ethanol.

In order to prepare phosphosilicate, Anastasescu, et al. (2006) used TEOS as SiO_2 source and triethylphosphite (TEPI), $\text{PO}(\text{C}_2\text{H}_5)_3$ and H_3PO_4 as a phosphorus source. TEOS diluted with EtOH, water containing HCl as catalyst and the appropriate amount of phosphorus precursor: TEPI, $\text{PO}(\text{C}_2\text{H}_5)_3$ and H_3PO_4 were added. The mixture was then stirred. Visiliu, et al. (2007) again use mixture of TEOS, EtOH, water, HCl and H_3PO_4 to produce phosphosilicate.

Jin, et al. (2007) prepared phosphosilicate by mixing TEOS, EtOH, water, HNO_3 and H_3PO_4 . A two-step catalysed hydrolysis process was employed to prepare phosphosilicate solution using TEOS, EtOH, distilled water containing HNO_3 . TEOS was mixed with EtOH and a stock solution of water and HNO_3 was added drop by drop with constant stirring. A solution of H_3PO_4 diluted with EtOH was added drop by drop at room temperature and stirred.

Avila, et al. (2008) also prepared phosphosilicate using sol-gel process. The composition of starting solutions was TEOS, phenyltriethoxysilane (PTES), ammonium phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) and ammonium hydroxide. The sols were prepared by adding the precursors to a mixture of ethanol, water and ammonium hydroxide. It was reported that Qiu, et al. (2008) had prepared phosphosilicate with high phosphorus content ($\text{P mol \%} > \text{S mol \%}$) using phytic acid (inositol hexakisphosphate, IP6), TEOS, EtOH and water. Phytic acid was mixed with EtOH and water at ambient temperature. After 20 minutes, TEOS was added through a syringe while stirring.

Of the three methods of doping, CVD is one of the earliest and most established methods. This method offers excellent process control since the surface concentration of dopant is dependent on the vapour pressure of the dopant source during predeposition and the solid solubility of the dopant in silicon (which is temperature dependent). Therefore, by controlling the vapour pressure of the dopant source and the predeposition temperature, precise level of doping can be achieved. Nevertheless, the use of poisonous and sometimes explosive dopant source will require extra safety precautions which made the process very expensive and dangerous.

Ion implantation also offers excellent process control where the number of implanted dopant atoms and the implanted depth can be precisely controlled but the fast projectile upon impact on the target inevitably induced defects in the target. Although, these defects can be annealed off but the biggest worry is over the ability of the annealing processes to completely eliminate the implant-induced damage. Besides that, the equipment is expensive and complex (Van Zant, 2000). It contains many safety hazards (example high voltage and toxic gases) to the personnel which operate and service the machine. To minimize the likelihood of accidents from operating and

maintaining such equipment, careful safety procedures must be established and strictly followed. Ion implanters are complex machines, among the most sophisticated systems in wafer manufacturing. In order to be effectively utilized they must be conscientiously operated, monitored, and maintained by well-trained personnel (Wolf & Tauber, 1986).

Spin-on dopants, on the other hand, offer a number of clear advantages over CVD and ion implantation for device fabrication. First of all, the spin on dopant is applied to the substrate at certain humidity which is very easy to setup. Secondly by doing away with vapour-phase processes, the need to use and metering of toxic gases (as in CVD) is eliminated. Furthermore, the application of spin-on dopant using spinner will mean that the uniformity of dopant source over the silicon substrate surface can be ensured even if the size of the substrate is increased. Hence, a more uniform doping over the whole substrate is obtained. This may be important for application such as solar cell fabrication since the trend is towards increasing the size of individual cell (Teh, 1988).

Moreover, phosphosilicate sol prepared by sol-gel technology are easy compared from preparation of all the other method of doping. Plus, it is cost effective because the temperatures required in the process are low, ($<100^{\circ}\text{C}$), and no delicate vacuum system is needed. Besides, because of its speciality of low temperature preparation, it results in minimized air pollution and prevent of reaction with containers, thus it maintain the purity of the material (Brinker & Scherer, 1990). In addition, the most popular precursors used in sol-gel technology is metal alkoxides. Metal alkoxides are frequently volatile and high purity products. (Carter & Norton, 2007).

2.4 Applications of phosphosilicate

Although phosphosilicate has been used for dopant purpose, it also can be used for other application. Properties of phosphosilicate make it useful in a variety of applications in semiconductor technology. Phosphosilicate is widely used as insulating layers in the manufacture of microelectronic devices. It is used as the dielectric layer between polysilicon and metal in logic device and between stacked capacitors and metal in memory devices. In addition, doped silicon oxide finds use in microelectromechanical systems (MEMS) as sacrificial planar layers (Muscat, et al., 2001).

Phosphosilicate is exclusively used for its function as an intermediate dielectric providing, due to the phosphorus presence, added capabilities for effective gettering of sodium and other rapidly diffusing metal ions which are detrimental to microelectronic devices, and to increase the etching rate (Nassau, et al., 1985). The addition of these dopants lower the temperature required to soften or to flow the glass layer. The lowering of this temperature minimizes the diffusion of contaminants in underlying layers, and minimizes defect sites and warpage (Walder & Boyle, 2008). Nevertheless, the ability of phosphosilicate to undergo viscous deformation at a given temperature is primarily a function of the phosphorus content in the phosphosilicate (Nassau, et al., 1985).

2.5 Selection for the research

From all the chemical use by other researcher, a mixture of TEOS, isopropanol, distilled water and phosphoric acid was chosen for this research because of their availability in the laboratory. Furthermore, all the chemical listed above are available commercially which make the material easy to be obtained. Moreover, phosphoric acid

was selected as a phosphorus precursor due to its better incorporation in the SiO_x matrix (Anatasescu, et al., 2006).

2.6 Summary

This chapter discussed the types of dopant used in semiconductor technology. This chapter also revealed some information about phosphorus dopant and method of doping. The ingredients of phosphosilicate by other research works were also presented. Besides being used as a dopant source, phosphosilicate also can be used for other purposes.

CHAPTER 3

THEORY

3.1 Introduction

This chapter presents the general principles and theories of various aspects involved in this project. It starts with an explanation on spin-on glass/ dopant (n-type) fabrication. Then, it continues with the fundamental theories for formation of doped region. Metal-semiconductor contacts are also addressed in this chapter.

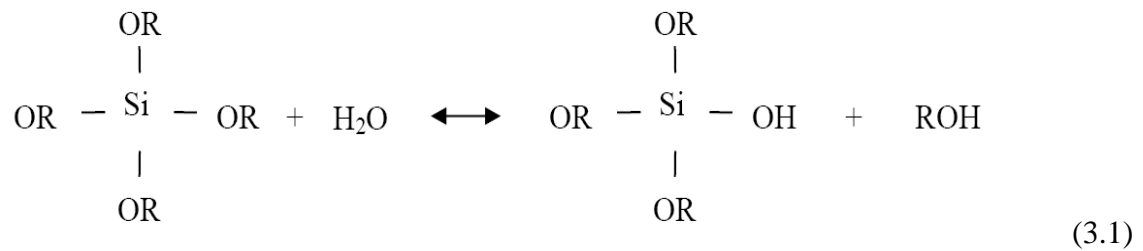
3.2 Spin-on glass/ dopant (n-type) fabrication

The SOG materials were prepared using sol-gel method. This technology is straightforward. The starting materials are silicon alkoxide or $\text{Si}((\text{OC}_2\text{H}_5)_4)$, water (H_2O), isopropanol ($((\text{CH}_3)_2\text{CH}(\text{OH}))$) and hydrochloric acid (HCl) as catalyzing acid (Brinker & Scherer, 1990). However, in order to make spin-on dopant (SOD) containing n-type impurities, e.g phosphorus in this case, phosphoric acid (H_3PO_4) was used instead of HCl as a catalyzing acid.

The fabrication of silica by means of the sol-gel method is based on the hydrolysis and polycondensation of silicon alkoxides such as tetraethylorthosilicate (TEOS) and tetramethoxysilane (TMOS). Both these compounds can be expressed as $\text{Si}(\text{OR})_4$, where R is the alkyl group. For TEOS $\text{R}=\text{C}_2\text{H}_5$ whereas $\text{R}=\text{CH}_3$ for TMOS. The silicon bonds with OR groups can easily be cleaved by water and therefore the above compound can easily be hydrolysed to yield hydroxyl derivatives in which the hydroxyl groups are attached to silicon atoms. Because TEOS and water are immiscible,

a mutual solvent which is isopropanol is normally used as a homogenizing agent and the reactions only begin when the solvent isopropanol is added (Nguyen, 1999).

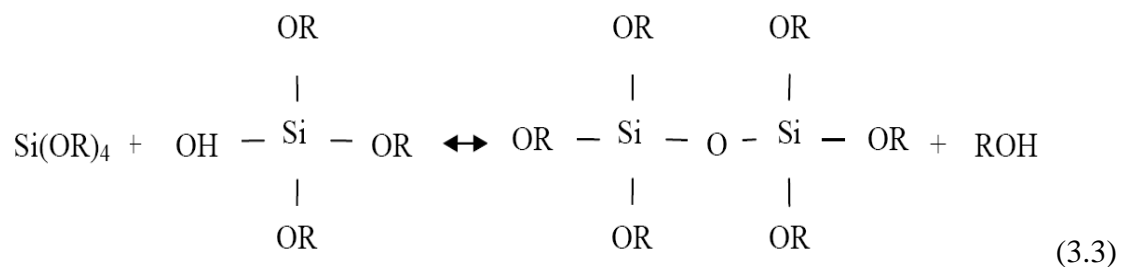
Hydrolysis is described by the reaction 3.1:



In the reaction 3.1, the alkoxy (OR) group is replaced by a hydroxyl group (OH) and alcohol is released as a by-product. If one adds a further water molecule hydrolysis will continue and as a result one further alkoxy group will be replaced. Overall the complete hydrolysis of a silicon alkoxide is described by the reaction 3.2.

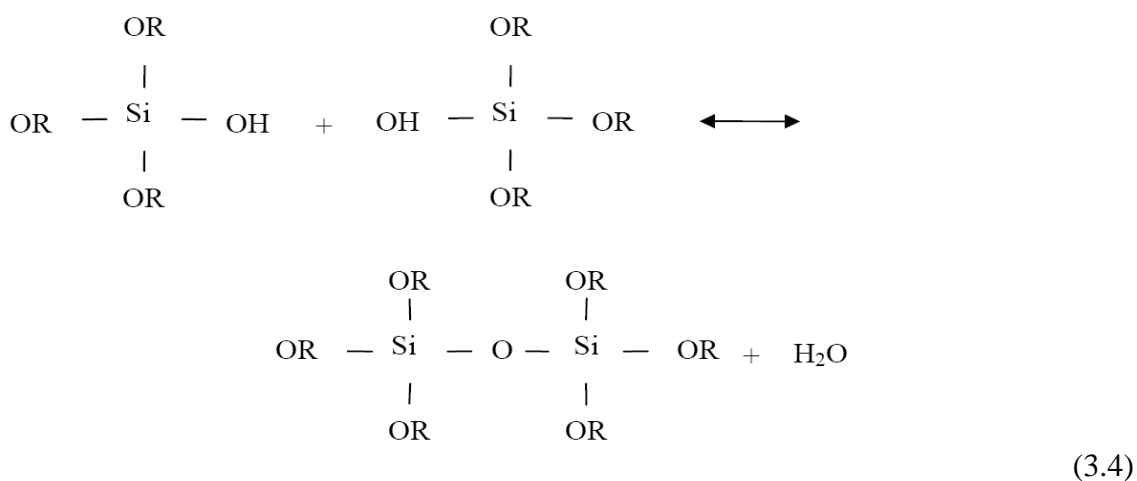


There are two parallel condensation reactions that take place in the sol. The first releases alcohol as a byproduct and is described by the reaction 3.3:



Reaction 3.3 is most commonly referred to as the weak condensation process. This process is not sufficiently strong to form a long chain gel structure. It shows, however, that condensation does take place even in the presence of a small quantity of water.

The most dominant condensation process takes place between one hydroxyl and one alkoxy group, giving water instead of alcohol as a byproduct. The importance of the reaction in the sol-gel process is immense since the excess water is then used to further hydrolyze alkoxy bonds according to reactions 3.1 and 3.2 (Darmstadt University of Technology, 2008):



The result of these hydrolysis and condensation reactions is the formation of colloidal suspension of particles in a liquid solution; the sol. All the reactions will continue with time even at room temperature and may result in dense sol of larger network polymers. If this happens the SOD will not be able to be applied uniformly on a substrate because of its very high viscosity. If allowed to continue, after some time, the sol will extend throughout in some random way to form a gel. In order to prevent these reactions the SOD should be stored at low temperature (Thompson, 2006).

3.3 Formation of doped region

IC fabrication is accomplished by selectively changing the electrical properties of silicon through the introduction of impurities commonly referred to as dopants. A major advance in semiconductor production was the development of diffusion doping techniques (Van Zant, 2000).

3.3.1 Dopant atom activation

A semiconductor is a material that can be tailored in such a way that it will conduct current in specified areas. The conductive properties are controlled by small concentrations of impurities, known as dopants. Silicon, the most common semiconductor, has four valence electrons; therefore it must either gain or lose four electrons to reach a stable state. The result is that silicon bonds with four other silicon atoms to create a stable structure. Dopant atoms change the conduction of the silicon by replacing one of the silicon atoms in the bonding arrangement. There are two types of impurities that can be used to change the conductive properties of a semiconductor; donors or acceptors. Donors are atoms that have five electrons in their outer orbital, and once inserted into the lattice, give this extra electron up to maintain a stable bonding configuration. This is illustrated in figure 3.1. This extra electron is then free to move about the crystal structure and can contribute to conduction. Since an electron is added to the system, this creates more negative charge carriers, therefore a region with a majority of donor atoms is known as n-type. Atoms used to create n-type regions are phosphorus, antimony, and arsenic; all group five elements on the periodic table.

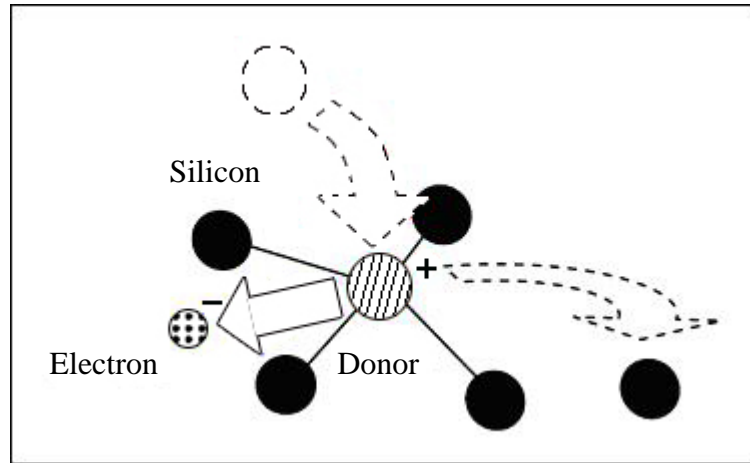


Figure 3.1: Atom substitutions as an activation mechanism (Woodard, 2006).

Similarly, acceptors are atoms that contain only three valence electrons. When these atoms replace silicon, they require an extra electron to achieve a stable bonding arrangement. This results in the contribution of a hole, or the absence of an electron, to the electrical conduction within the silicon. The hole is a positive charge carrier, therefore the region with mostly acceptor atoms is known as p-type. The atoms that can be used to create p-type regions are boron and indium.

There are several different choices for atoms to create either n-type or p-type regions in silicon. These atoms have different sizes, masses and bonding properties. Some atoms fit better in the silicon lattice. Arsenic fits in the silicon lattice best of all dopant atoms, therefore a higher concentration of arsenic atoms can be placed into the silicon crystal without having them form precipitates. In addition, the greater the mismatch between the dopant and the lattice, the more strain will be induced on the crystal structure, causing the formation of defects (stacking faults and dislocations) as the doping concentration is increased.

The method of activating dopant atoms is a process referred to as annealing. Energy in the form of heat is applied to the semiconductor. This energy must be sufficient to allow the dopant atoms to displace the silicon and form bonds with its neighbors. The temperature of the anneal process is a primary factor in determining how many of the dopants activate. In general, as the temperature increases, the amount of activation also increases. However, there are several factors that complicate this process. The amount of dopant in the silicon, referred to as the dose, actually affects the amount of dopants that activate. Figure 3.2 shows literature data for activation of boron at isochronal or constant time, annealing conditions.

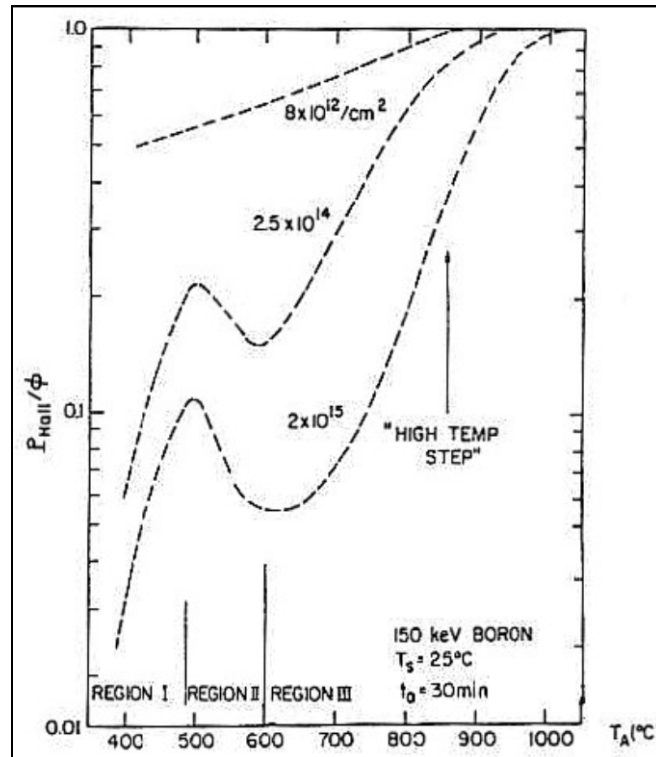


Figure 3.2: Temperature activation effects (P_{Hall} refers to the measured Hall dose) (Wolf & Tauber, 1986).

Note the decrease in activation around 600°C; this de-activation is due to formation of dislocations in the lattice, at which dopants can segregate (Wolf & Tauber,

1986). High temperature processing is required to remove these defects, as they can only be removed by a re-ordering of the lattice. Therefore it is critical in investigating low temperature activation that these defects do not form, as they cannot be removed (Woodard, 2006).

3.3.2 Fick's law of diffusion

In 1855, Fick developed his theory of diffusion on the analogy between material transfer in a solution and heat transfer by conduction. Fick's first law states that in the absence of convection the local rate of transfer of solute atom per unit area (i.e the diffusion flux) is proportional to the concentration gradient in the direction of transfer at that point. In one-dimension,

$$J = -D \frac{\partial N}{\partial x} \quad (3.5)$$

where J is the rate of solute transfer (i.e diffusion rate), N is the concentration of solute at the point x , and D is the diffusivity.

Fick's second law which is the law of conservation of matter, states that the change of solute concentration with time must be equal to the decrease in diffusion flux, i.e,

$$\frac{\partial N}{\partial t} = -\frac{\partial J}{\partial x} \quad (3.6)$$

where t is time. Substituting equation (3.5) into (3.6) gives

$$\frac{\partial N}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial N}{\partial x} \right) \quad (3.7)$$

Equation (3.7) can be solved for various diffusion conditions by considering the corresponding initial and boundary conditions to obtain $N(x,t)$, the solute concentration at the point, x and time, t (Teh, 1988).

3.3.3 Diffusion process

Diffusion is the process by which a species moves as a result of the presence of a chemical gradient. It is a natural chemical process with many examples in everyday life (Van Zant, 2000). The diffusion of controlled impurities or dopants into Si is the basis of p-n junction formation and device fabrication. In the doping of silicon by diffusion, the silicon wafer is placed in an atmosphere containing the impurity or dopant to incorporate. Because the silicon does not initially contain the dopant in its lattice, two regions with different concentrations of impurities and diffusion can therefore occur, as schematically illustrated in figure 3.3.

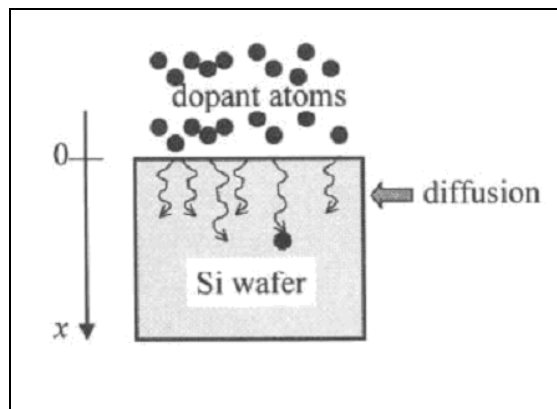


Figure 3.3: Diffusion of dopants in a silicon wafer

There exist several diffusion mechanisms. An impurity can diffuse into an interstitial site in the lattice and can move from there to another interstitial site, as shown in figure 3.4(a). For interstitial diffusion, sometimes a silicon atom can be knocked into

an interstitial site, leaving a vacancy in the lattice where a diffusing dopant atom can fit, as shown in figure 3.4(b). A third mechanism is possible which consists of a dopant directly diffusing into a lattice vacancy (figure 3.4(c)) which is substitutional diffusion. It is only in the last two cases that an impurity occupies a vacated lattice site that n-type or p-type doping occurs.

There are two major techniques for conducting diffusion, depending on the state of the dopant on the surface of the wafer: (1) constant-source diffusion, also called predeposition or thermal predeposition, in which the concentration of the desired impurity at the surface of the semiconductor is kept constant; and (2) limited-source diffusion, or drive-in, in which a fixed total quantity of impurity is diffused and redistributed into the semiconductor to obtain the final profile.

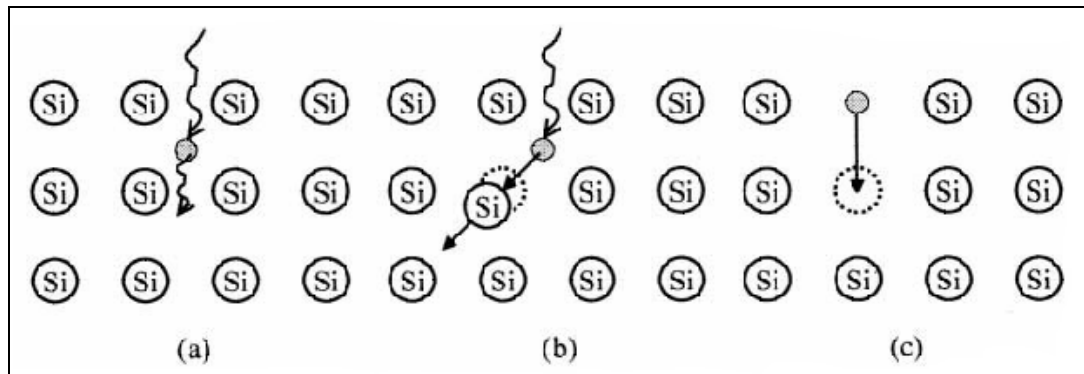


Figure 3.4: Three possible diffusion mechanisms in a silicon wafer (Razeghi, 2006).

3.3.3 (a) Constant-source diffusion: predeposition

During predeposition, the silicon wafer is heated to a carefully selected and controlled temperature, and an excess of the desired dopant is maintained above the wafer. The dopants diffuse into the crystal until their concentration in it near the surface is in equilibrium with the concentration in the surrounding ambient above it. The